



Developing Rigid Polymer Electrolytes

by James F. Snyder

ARL-RP-188

September 2007

*A reprint from Polymer Preprints, Vol. 45, No. 2, August 2004,
American Chemical Society, Philadelphia, Pennsylvania, 22-26 August 2004.*

NOTICES

Disclaimers

The findings in this report are not to be construed as an official Department of the Army position unless so designated by other authorized documents.

Citation of manufacturer's or trade names does not constitute an official endorsement or approval of the use thereof.

Destroy this report when it is no longer needed. Do not return it to the originator.

Army Research Laboratory

Aberdeen Proving Ground, MD 21005-5069

ARL-RP-188

September 2007

Developing Rigid Polymer Electrolytes

James F. Snyder

U.S. Army Research Laboratory

Weapons and Materials Research Directorate

*A reprint from Polymer Preprints, Vol. 45, No. 2, August 2004,
American Chemical Society, Philadelphia, Pennsylvania, 22-26 August 2004.*

REPORT DOCUMENTATION PAGE			<i>Form Approved</i> <i>OMB No. 0704-0188</i>		
Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing the burden, to Department of Defense, Washington Headquarters Services, Directorate for Information Operations and Reports (0704-0188), 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to any penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number. PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ADDRESS.					
1. REPORT DATE (DD-MM-YYYY) September 2007		2. REPORT TYPE Reprint		3. DATES COVERED (From - To)	
4. TITLE AND SUBTITLE Developing Rigid Polymer Electrolytes			5a. CONTRACT NUMBER		
			5b. GRANT NUMBER		
			5c. PROGRAM ELEMENT NUMBER		
6. AUTHOR(S) James F. Snyder			5d. PROJECT NUMBER		
			5e. TASK NUMBER		
			5f. WORK UNIT NUMBER		
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) U.S. Army Research Laboratory ATTN: AMSRD-ARL-WM-MA Weapons and Materials Research Directorate, Aberdeen Proving Ground, MD, 21005-5069.			8. PERFORMING ORGANIZATION REPORT NUMBER ARL-RP-188		
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) U.S. Army Research Laboratory 2800 Powder Mill Road Adelphi, MD 20783-1197			10. SPONSOR/MONITOR'S ACRONYM(S)		
			11. SPONSOR/MONITOR'S REPORT NUMBER(S) ARL-RP-188		
12. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release; distribution is unlimited.					
13. SUPPLEMENTARY NOTES					
14. ABSTRACT This report is a reprint of a paper published in Polymer Preprints, Vol. 45, No. 2, by the American Chemical Society in Fall 2004. The focus of this research is the synthesis and characterization of highly conductive rigid polymer electrolytes. Traditional solvent-free polymer electrolytes allow for long-range ion diffusion by means of ion-polymer coupling in the amorphous phase of the polymer host. Coupled systems typically require low glass transition temperatures for fast ion diffusion, resulting in poor mechanical properties when fillers are not added. The effort described here explores polymer electrolytes in which ion diffusion is decoupled from polymer motion. These materials allow for the development of polymers with desirable structure and fast ion transport at low temperatures. This is accomplished through the design of high dielectric polymer hosts with large internal free volume. The recently reported step polymerization using vinylene carbonate and oxalic acid derivatives was modified to eliminate the formation of a dominant byproduct, and extended to include more robust but less reactive monomers, including derivatives of 3-sulfolene, maleimide, and malonic acid.					
15. SUBJECT TERMS					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT SAR	18. NUMBER OF PAGES 8	19a. NAME OF RESPONSIBLE PERSON James F. Snyder
a. REPORT U	b. ABSTRACT U	c. THIS PAGE U			19b. TELEPHONE NUMBER (Include area code) (410) 306-0842

DEVELOPING RIGID POLYMER ELECTROLYTES

James F. Snyder

U.S. Army Research Laboratory, AMSRD-ARL-WM-MA,
Aberdeen Proving Ground, MD 21005

Introduction

Polymer systems have undergone development in recent years for use as electrolytes in modern power source applications such as fuel cells and secondary batteries.¹ Polymer electrolytes have many physical advantages over other types of electrolytes, including the ability to be modified to exhibit a broad range of mechanical properties and the ability to be cast into thin films for use in portable or flexible applications. Significant focus in the literature has been to improve electrochemical performance while maintaining reasonable mechanical properties.² Less attention has been given to providing enhanced structural properties to the membrane. One reason for this concerns the mechanisms for ion diffusion in polymer systems. Ion diffusion in solvent-free polymer electrolytes has been shown to occur by means of short-range ion hopping between coordination sites, and long-range diffusion dependent on segmental motion of the polymer host.³ An increase in polymer segmental mobility, reflected in depression of the polymer glass transition temperature, generally leads to an increase in ion conductivity and a decrease in polymer structure. An apparent inverse relationship exists between rigid structure and ion diffusion for solvent-free polymer electrolytes.

A common solution to providing enhanced electrochemical properties has been to add plasticizers to thin film membranes. The addition of liquid plasticizers to polymer scaffolds such as PVDF results in gels with high ion conductivities.⁴ However, gels have added complications with solvent flammability and solvent management. The addition of small particle inorganic plasticizing fillers to solvent-free polymers typically results in more robust membranes, but conductivities are lower than those observed in gels.⁵ Another method for developing structural electrolytes involves the synthesis of high dielectric polymers with rigid architecture that have a large internal free volume and ion diffusion decoupled from polymer motion.⁶ Although a solvent-free and particle-free highly conductive rigid polymer electrolyte is still unreported, several advances have been made in designing these systems. Examples include glassy electrolytes,⁷ polymer-in-salt systems,⁸ and polymers based on common solvents such as poly(vinyl alcohol)⁹ and poly(vinyl carbonate)¹⁰. The project presented here is based upon the latter technology.

Experimental

Materials. All of the reagents used in this study were purchased from Alpha Aesar and used without further purification, except where noted.

Methods. Step polymerization of cyclic monomer vinylene carbonate or 3-sulfolene with oxalic acid or malonic acid was attempted by chemical reaction according to method described in the literature,¹⁰ with variations as described below. The anticipated polymers are shown in Figure 1.

Cyclic monomers, including vinylene carbonate and 3-sulfolene, were quantitatively brominated on a 10 g scale using 1.2 molar equivalent of liquid bromine in 50 mL of carbon tetrachloride (vinylene carbonate) or 50 mL of 40% chloroform in carbon tetrachloride (3-sulfolene). The variation in reagent polarity accounts for the different choice of solvent. Dibromovinylene carbonate (**1**) was purified by distillation under vacuum. Dibromosulfolene (**2**) was purified by recrystallization from methanol.

Silver salts of the diacid monomers were accomplished by addition of silver nitrate. Silver oxalate is known to precipitate very quickly out of an aqueous solution of silver nitrate and oxalic acid. Silver malonate is largely unreported and was found to proceed at less than 5% yield using the above method. Addition of a quantitative amount of triethylamine (TEA) to the malonic acid/silver nitrate solution using dry acetonitrile as a solvent resulted in 100% yield of white powder that was subsequently filtered and washed with acetonitrile. Exposure of the reagents to water or light during reaction resulted in an inert brown solid. However, after washing the white solid product with acetonitrile, exposure to water or light had no effect.

Step polymerization was attempted by addition of a silver diacid salt to either of the brominated reagents. The choice of solvent and reaction conditions yielded different products, as described below, but 50/50 DMF/water was used initially. Reactions employing vinylene carbonate derivatives were found to be most successful at room temperature, whereas reactions employing derivatives of 3-sulfolene were found to be inhibited at room temperature but to generate sideproducts above 70 °C.

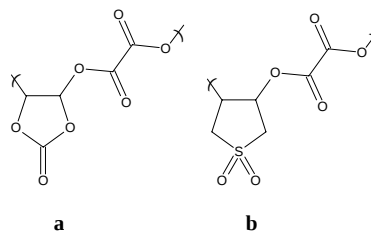


Figure 1. Polymers PVICOX (a) and PSOX (b)

Results and Discussion

The literature reaction to form the AB polymer of vinylene carbonate and oxalic acid,¹⁰ referred to as PVICOX and shown in Figure 1a, was explored in depth and extended to less reactive monomers to form compounds such as that in Figure 1b, referred to as PSOX. Reaction between a brominated cyclic alkene and the silver salt of a diacid is not evident elsewhere in the literature and is of interest for development of similar materials.

The reaction under the reported conditions was found to apparently proceed to a nonpolymer byproduct exhibiting properties similar to those expected of PVICOX. Characterization is similar to that reported of PVICOX, including DSC of the pure polymer and impedance measurements of the polymer mixed with lithium triflate. However, repeating the reaction with substitution of vinylene carbonate by 3-sulfolene to form PSOX also resulted in generation of the same product. In some cases, small amounts of minor product was collected that may correspond to the expected polymers. Apparent byproduct of the cyclic reagent was also recovered. Analysis of the major product was undertaken to evaluate the side reaction that occurred and correct for it.

Increases in temperatures appear to reduce the yield of all products by catalyzing the decomposition of silver oxalate. However, temperatures higher than 50°C were necessary to catalyze reactions involving the 3-sulfolene derivative. GPC analyses of the major product were inconclusive, although no evidence was found for polymer above MW 1000. Extensive ¹³C NMR using a Bruker 600 MHz AVANCE system revealed only two peaks in the major product, δ 161 (quaternary carbon) and δ 45 (CH₃). The quaternary peak corresponds to oxalate, but the absence of peaks corresponding to vinylene carbonate further suggest that the cyclic reagents are not included in the major product. The carbon peak at δ 45 is unknown. ¹H NMR revealed only one peak, δ 2.5 (s), apparent through comparison of individual spectra generated using water-d₄ and DMSO-d₆ as solvents. Comparison was made to the theoretical spectra of a variety of oxalate and urea derivatives using ChemDraw's NMR prediction capabilities. It was found that both the ¹³C and ¹H NMR spectra exactly match the expected spectra for tetramethyloxamide, the dimer form of DMF.

Since the reagents may have reacted with the solvent, the solvent system was varied from the DMF/water solution. The only two systems found to appreciably sustain reaction were DMAC/water and DMSO/water. In both situations the unknown byproduct described above was not observed. The resulting products had NMR spectra similar, but not exactly corresponding, to those expected of the polymers.

Table 1 lists the results from elemental analysis. The data in Table 1 was generated using a Perkin Elmer Series II CHNS/O Analyzer, model 2400, in CHNS mode. Samples were dried under vacuum to constant mass prior to analysis. Each data point is an average over two samples. Deviation from the average was limited to $\pm$ 0.5 wt% for each data point. The mass that is unaccounted for may be attributed primarily to oxygen. The sulfur content in samples 1-3 correspond to a very low number of sulfur atoms and may be attributed to artifacts or noise. This is particularly true for trial 1, in which no sulfur bearing compound was introduced into the reaction. Comparing sample data taken from the brominated sulfolene reagent with the theoretical expectations confirms that the instrument is accurate at moderate sulfur content.

The results in Table 1 support the hypothesis that silver oxalate reacts with DMF to form a byproduct. The data in trials 1 and 2 are within experimental error of each other, and the hydrogen and nitrogen contents are very different from those expected of PVICOX or PSOX. Residual DMF or water cannot account for the discrepancy, and the samples were prepared in such a way that there is little residual solvent expected. The data does not correlate exactly to that expected of tetramethyloxamide either, but it is a much better fit. The product is still considered to be unknown at this time and further tests are underway.

Switching the solvent appears to eliminate formation of the unknown product. Trials 3 and 4 show a much different elemental ratio than trials 1 and 2, and they are also different from each other. Although they do not correspond exactly to the expected spectra for PVICOX or PSOX, they are a better fit. These products are also considered to be unknown at this time and further tests are underway.

Table 1. Sample Properties by Elemental Analysis

Trial	Cyclic Monomer	Solvent	% C	% H	% N	% S
1	Vinylene carbonate	DMF/H ₂ O	34.7	6.1	9.1	2.3
2	Sulfolene	DMF/H ₂ O	32.6	6.1	9.4	2.3
3	Vinylene Carbonate	DMSO/H ₂ O or DMAC/H ₂ O	35.7	5.0	3.5	2.0
4	Sulfolene	DMAC/H ₂ O	50.3	4.2	3.5	21.6
Sample: 3-sulfolene, brominated (Theoretical)			17.3 (17.3)	2.0 (2.2)	0 (0)	11.3 (11.5)
Theoretical: PVICOX (dihydrate)			34.5 (28.6)	1.2 (2.9)	0 (0)	0 (0)
Theoretical: PSOX (dihydrate)			34.6 (29.8)	2.9 (4.2)	0 (0)	15.6 (13.3)
Theoretical: Tetramethyloxamide (dihydrate) (tetrahydrate)			50 (40.0) (33.3)	8.4 (9.0) (9.3)	19.4 (15.6) (13.0)	0 (0)

Conclusions

Reactions between dibromo-substituted cyclic alkenes and diacid silver salts were explored as possible means to step polymerization. Apparent problems with published reaction conditions were elucidated and possibly eliminated. Further characterization of the products is underway. Further variation of both reagents is also underway, with particular emphasis on replacement of oxalate with malonate. Due to less activation of the end groups, malonate is found to react less readily than oxalate and requires addition of nonprotic bases such as triethylamine or pyridine to advance the reaction at room temperature.

Acknowledgements. I would like to thank the National Research Council for funding this project. I also wish to thank Dr. Kang Xu and Dr. Richard Jow in the Battery Team of ARL for their continuing support involving the electrochemical measurements, and to Dr. Josh Orlicki for helpful discussions.

References

- (1) Ciuffa F., Croce F., D'Epifanio A., Panero S., Scrosati B. *J Power Sources* **2004**, 127(1-2), 53.
- (2) Meyer, W.H. *Adv. Mater.* **1998**, 10(6), 439.
- (3) Berthier, C.; Gorecki, W.; Minier, M.; Armand, M.B.; Chabagno, J.M.; Rigaud, P. *Solid State Ionics* **1983**, 11, 91
- (4) Song J.Y.; Wang Y.Y.; Wan C.C. *J. Power Sources* **1999**, 77 (2), 183
- (5) Scrosati, B; Croce, F; Panero, S. *J. Power Sources* **2001**, 100 (1-2), 93.
- (6) Imrie, C.T.; Ingram, M.D.; *Electrochim. Acta* **2001**, 46, 1413.
- (7) Forsyth, M.; Jiazeng, S.; MacFarlane, D.R. *Electrochim. Acta.* **2001**, 45, 1249.
- (8) Angell, C.A.; Lin, C.; Sanchez, E. *Nature* **1993**, 362, 137.
- (9) Yamamoto, T.; Inami, M.; Kanabara, T. *Chem. Mat.* **1994**, 6, 44.
- (10) Wei, X.; Shriver, D.F. *Chem. Mat.* **1998**, 10, 2307.

Distribution List

ADMNSTR 1 elec
DEFNS TECHL INFO CTR
DTIC OCP (ELECTRONIC COPY)
8725 JOHN J KINGMAN RD STE 0944
FT BELVOIR VA 22060-6218

US ARMY RSRCH LAB 6
IMNE ALC IMS MAIL & RECORDS MGMT
AMSRD ARL D J M MILLER
AMSRD ARL CI OK TL TECHL LIB (2 COPIES)
AMSRD ARL CI OK T TECHL PUB (2 COPIES)
2800 POWDER MILL ROAD
ADELPHI MD 20783-1197

US ARMY RESEARCH LAB 1
AMSRD CI OK TP TECHL LIB
ATTN T LANDFRIED
APG MD 21005

US ARMY RESEARCH LAB 1
AMSRD ARL WM MA J SNYDER
BUILDING 4600
APG MD 21005-5069

TOTAL 9 (1 Electronic, 8 HCs)

INTENTIONALLY LEFT BLANK.